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SOURCE Zhurnal Prikladnoy Khimii, Vol XX, No 11, 1947.THIRTY YEARS OF THE USSR FERTILIZER AND SULFURIC ACID INDUSTRY

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The basic chemical industry of the USSR and its mightiest branch, the fertilizer industry, in particular, have made gigantic strides in the Stalin five-year plans. In prerevolutionary Russia there existed only a few small superphosphate and sulfuric acid plants which for the most part used imported raw materials. Nitrogen and potassium industries were nonexistent. The agricultural regions, with the exception of the west and partly the southwest, did not use any mineral fertilizers, and the average amount of fertilizer per unit of cultivated area was the lowest in Europe.

Concepts that the natural and historical conditions of Russian agriculture were unique, and that the use of mineral fertilizers was inadvisable, were widespread in the agronomic circles of those days. Experiments with fertilizers carried out by Mendeleev, Engelhardt, Timiryazev, and others at the end of the 19th and the beginning of the 20th centuries did not affect the majority of the peasants. On the other hand, the agronomists knew very little of, and were not much interested in, agricultural chemistry; therefore, with a few exceptions, they did not publicize the use of mineral fertilizers.

Among Russian industrialists, whose knowledge of mineral fertilizers was limited, the opinion was prevalent that the Russian phosphorites, except for small deposits in the Podol'sk region, were of poor quality and unsuitable for chemical conversion into fertilizers. The opinion also prevailed that there were no potash deposits either in Russia or in other countries, except in Germany. Fertilizers were studied only at two or three universities.

How far removed that time seems now, after 30 years, when our country had discovered immense deposits of agricultural ores, constructed tremendous plants for the production of phosphorus, nitrogen, and potassium fertilizers, trained thousands of chemists, engineers, and agronomists, who enthusiastically developed the fertilizer industry and its technical application to socialistic agriculture. A gigantic step has been taken, and a tremendous amount of constructive and creative work has gone into it.

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A comparison of the increase in the Soviet and foreign fertilizer industries during the three five-year plans leads to the same conclusion. The history of industrialization and technical development of other countries does not show any such rapid growth, with production capacities increasing tenfold and over, and gigantic mines and fully developed chemical plants appearing in entirely new regions, far from the center of the country, such as Khibiny, Solikamsk, Western Siberia, Uzbekistan, and others.

Since the development of the national structure had been based on a planned socialistic economy, science with its analyses, generalizations, and prognoses had a decisive effect on the progress of the fertilizer industry. The Higher Council of National Economy (VSNKh) created the scientific and technical division (NTO) which in 1918-1919 founded the Scientific Institute of Fertilizers (NIU) as one of the first scientific research institutes in the country. In 1933 the Institute of Insectofungicides was combined with the NIU, and the combined institute has been given the name of Scientific Institute of Fertilizers and Insectofungicides (NIUIF). This institute was essentially organized by the departments of the Public Committee on Fertilizers, which had been founded in 1916-1917 and which included a number of agriculturists, geologists, chemists, and engineers. It may thus be asserted that the NIUIF is a contemporary of the October Revolution.

The Institute of Fertilizers, like the Karpov Institute and the Leningrad Institute of Applied Chemistry, is the oldest and largest Institute of learning of the Soviet chemical industry. The NIU has been headed by the foremost scientists of the country, enthusiastic supporters of chemistry in national economy, Ya. V. Samoylov (geologist), E. V. Britzke (chemical engineer), and D. N. Pryanishnikov (agricultural chemist). The NIU was planned and organized as a complex institute in which all problems relating to fertilizers, beginning with the study of the raw materials and their technical treatment, and ending with the conditions for the efficient application of fertilizers in agriculture, have been studied collectively from all angles. The institute grew by leaps and bounds and soon there were a number of sections, bases, an experimental plant, and experiment stations. Numerous mining and geological surveys of agronomic ores have been carried out. The Institute has worked in close cooperation with industrial organizations, and scientific and planning commissions. The NIU has taken active part in the construction of large and modern enterprises, such as the Khibinsk Apatite Combine, the Solikamsk Potash Combine, the Voskresensk, Chernorechensk, and Aktyubinsk fertilizer enterprises, and many other mines and plants.

As the work of the NIU progressed, new institutes were organized, with many members of the NIU transferring to them. These included the State Institute of Nitrogen Industry (GIAP), All-Union Institute of Fertilizers, Agrotechnology and Agricultural Soil Science (VNIIA), and State Institute of Mining-Chemical Raw Materials (GIGKhS). Many plant research laboratories which also contributed to the development of the chemical technique were founded.

As soon as the Civil War (1920-1921) began to abate, two Moscow schools of higher learning, the Institute of National Economy and the Moscow Technical Institute, organized departments for the study of mineral fertilizers. Later similar departments were founded in other cities, such as Leningrad, Khar'kov, Odessa, and others.

The research organizations and universities mentioned above carried out such a tremendous amount of work that it may be stated without exaggeration that all the large and small new developments, and radical improvements in the methods of producing fertilizers and sulfuric acid, were based on the results of their scientific study. It is noteworthy that in the first period of mobilization of the scientific forces for attacking the problems of mineral fertilizers (1919-1923), the major efforts of the scientists were directed towards determining the agricultural efficiency of fertilizers and to proving

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their tremendous importance in the economy of the Soviet agriculture. In subsequent years, pot and field tests with fertilizers in various regions and with various crops made it possible to determine the required assortments of fertilizers and the geographical distribution of the manufacturing plants under all the five-year plans. Geological research and surveys of phosphate deposits increased greatly in 1923-1924. Those relating to potash salts began in 1925-1926.

Before 1926-1927, the chemical engineers were concerned largely with studies of the conversion of numerous low-grade phosphorites to superphosphate and concentrated fertilizers. Extensive construction of large plants and experiments on a large-plant scale began in 1938 for the purpose of utilizing Khibin apatites and Solikamsk potash salts. Furthermore, erection of the first installations for the fixation of atmospheric nitrogen, that is, for the production of synthetic ammonia and calcium cyanamide, began in that year.

Large nitrogen, phosphate, and potassium combines were erected in the First and Second Five-Year Plans (1928-1932 and 1932-1937). The development of the Stakharov movement among industrial and kolkhoz workers, which was particularly marked from 1934 to 1936, played an important role in the fulfillment and surpassing of the Second Five-Year Plan. It also had a tremendous influence on the further growth of the fertilizer industry, on the increase of commercial crops, and on raising the creative level of industrial work.

In 1938, the 18th Conference of VKP(b) proclaimed the Third Five-Year Plan, "the five-year plan of chemistry," and outlined the program for the construction of mineral fertilizer plants. The war with German fascism, which began in 1941, not only stopped construction but caused tremendous losses in the nitrogen and phosphate industries located in the west and south of the country. The production of fertilizers decreased markedly during the war.

The new Five-Year Plan, 1946-1950, for the recovery and development of our national economy, provides not only for the reconstruction of fertilizer plants destroyed or damaged during the war, but also for the erection of many new nitrogen, phosphorus, and potassium plants, as well as for the development of mines, to provide all the mineral fertilizers required for commercial crops (cotton, long-fiber flax, hemp, beet sugar, rubber-bearing plants, tobacco, tea, and citrus trees) and to increase the use of mineral fertilizers for other crops, particularly vegetables and potatoes (Law on the Five-Year Plan for Reconstruction and Development of the National Economy of the USSR 1946-1950). With this in view, the law provides for an increase in the production of mineral fertilizers to guarantee by 1950 the production of twice as much phosphate fertilizer, 1.8 times as much nitrogenous fertilizer, and 1.3 times as much potassium fertilizer as produced before the war. At the same time, provision is made for the construction of large fertilizer works in line with the Five-Year Plan.

The assortments of the various fertilizers, particularly of concentrated and complex fertilizers, will be increased by applying new and modern methods of production. The Fifth Five-Year Plan also provides for an increase and a further development of processes for the production of sulfuric acid, which is closely related to the growth of the superphosphate and other fertilizer industries.

Agricultural Ores and Other Types of Raw Materials

In the past 30 years the Soviet geologists discovered tremendous deposits of phosphorites, amounting to 40 percent of the world's reserves of phosphatic raw materials. For this reason the Soviet Union occupies first place with respect to world deposits of phosphatic raw materials. In pre-revolutionary Russia, the majority of phosphorite deposits had neither been discovered nor surveyed. In 1913, the phosphate deposits, more or less known

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but not thoroughly investigated, were estimated at 20 to 30 million tons, and mining averaged 20,000 to 30,000 tons per year.

Geological surveys made shortly before the revolution found that Russia possessed very large deposits of phosphorite ores. However, these were distributed over a large area and contained relatively low amounts of P_2O_5 in the presence of large amounts of Al_2O_3 and Fe_2O_3 .

Large-scale surveys to determine the resources of industrial phosphorites were started by the Soviet government. In this tremendous undertaking, the honorable role of guidance belonged to Ya. V. Samoylov (up to 1925) and to members of the NIU. All the geological surveys were carried out by that Institute under the direction of Ya. V. Samoylov, A. D. Arkhangel'skiy, and A. V. Kazakov, M. P. Fivog, I. M. Kurman, B. M. Gimmel'farb, P. L. Bezrukov, and others. The progress made in the geological surveys of phosphorite deposits is illustrated by the following figures: the area studied covered more than 200,000 square kilometers and more than 250 surveying groups participated. As a result, the total deposits of phosphate ores in the USSR are at present estimated at several billion tons.

Since the Soviets came into power many new deposits have been discovered while others have been surveyed and put in operation. These include the Yagor'sk, Upper-Kama, Aktyubinsk, Saratov, Krolevets, and many other deposits of pebble phosphorites. The reserves of phosphate ores in the USSR increased markedly with the discovery of extensive new deposits of apatite in the Khibins and of blanket deposits of phosphorites, a new type for the USSR, in the mountains of Kara-Tau (southern Kazakhstan).

The detailed study and the industrial exploitation of apatite on the Kola peninsula under the difficult geographic conditions of the Arctic was carried out by the directed, planned, and collective work of a great number of geologists, mining engineers, chemists, technologists, construction engineers, and other experts. To foreign experts, the mastering of such a gigantic deposit in such a short time under the conditions of the uninhabited Arctic area was an astonishing accomplishment. Some of the foreign firms, who had tested apatite as a raw material for the production of superphosphate, reported at the time that it was unsuitable for that purpose (as is known, they later changed their opinion).

The Soviet experts had shown that they were able to accomplish that which the representatives of the capitalist world did not think to be possible. Based on the surveys of mineralogical and geological expeditions of the Academy of Sciences under the direction of A. E. Fersman, research work on a large scale was instituted by the NIU on Kukisvumchorr Mountain of the Khibins in the spring of 1929. This work was carried out continuously for 3 years (1929-1932) under exceptionally difficult conditions of the mountainous North by a large staff (about 400) under the general guidance of M. P. Fivog. The area of the apatite deposits investigated by the Institute covered about 20 kilometers. The first to be investigated in detail was the Kukisvumchorr-Yuksorsk section which contained large deposits of rich speckled apatite ores. A very large mine was then prospected and exploited on the basis of the data obtained.

The distinctive characteristics of apatite as compared to phosphorite (crystalline structure, larger particle size, absence of organic impurities and carbon dioxide, presence of rare earths, etc.) required a treatment (flotation) of the apatite-nepheline ores which differed from that used on orogenic phosphorites. The studies of the NIU and Mekhanchor prompted the construction of a flotation plant for the separation of apatite from nepheline and other minerals. Flotation of apatite ores yields a concentrate containing as much as 40 percent P_2O_5 , which is thus the richest phosphatic raw material in the world. The flotation plant of tremendous capacity erected at the mine made possible the utilization of this raw material for the production

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of high-grade superphosphate containing 40 to 50 percent of available P_2O_5 and of phosphorus, phosphoric acid, concentrated fertilizers, and many salts. For many years now apatite has also been exported to other countries.

The discovery, by Soviet investigators, of the tremendous blanket deposits of phosphorites in the mountains of Kara-Tau (Dzhambul'sk district of the Kazakh SSR) was also an event of great importance. Beginning in 1936, with the geological material collected by I. I. Mashkar in 1935 in the basin of the Kyr-Chabakta River, the Kara-Tau range was thoroughly investigated by the geologists of the NIUIF under the direction of P. L. Bezrukov and B. M. Gimul'farb. Large-scale geological, hydrogeological, and topographical studies resulted in the discovery of a basin containing phosphorites which in quantity and quality of the phosphorite layers exceeds all other phosphorite deposits of the USSR. With the discovery of these deposits, the Soviet Union acquired in Central Asia a large phosphate base which contains about 12 percent of all the phosphate reserves of the USSR. This deposit stretches along the Kara-Tau range in several parallel stripes 120 kilometers long and from a few to 25 meters wide.

The P_2O_5 content in the phosphate patches of the most thoroughly investigated district (Chulak-Tau) varies between 14 and 30 percent and reaches 33 to 35 percent in some sections. The ore also contains 1 to 12 percent CO_2 , 1.5 to 2.5 percent $(AlFe)_2O_3$, and 5 to 60 percent insoluble residue. The average P_2O_5 content (28 percent) is about 14 times the average Fe_2O_3 content (2 percent), thus making the Kara-Tau phosphorites suitable for chemical treatment.

The properties of the Kara-Tau phosphorites are better than any of the other USSR phosphorites and inferior only to the Khibin flotation apatite concentrate. The mining and chemical combine of Kara-Tau has already started the exploitation of this deposit. Thus, a substantial base has been created in Kazakhstan for supplying high-grade raw material to the new phosphate fertilizer plants of Central Asia and other adjacent regions.

Soviet geologists and chemists have won another historical battle, the discovery and exploitation of the largest potash salt deposits in the world, in the Solikamsk region of the northern Urals.

For many decades Germany held a monopoly, supplying all countries of the world with potash salts. Up to the early thirties of the present century, Stassfurt and Alsace potash salts reigned supreme in the world market. Only a few scientists, basing their conjectures on physicochemical and geochemical analyses, were convinced that the Solikamsk region contained large deposits of sylvinite and carnallite. Among these scientists, N. S. Kurnakov, Ya. V. Samoylov, P. I. Preobrazhenskiy, and a number of collaborators were the pioneers of the Soviet potash industry.

Experience confirmed the prognosis of the Soviet scientists, and in September 1925 a mining and geological party under the direction of P. I. Preobrazhenskiy discovered, at the depth of 90 to 100 meters in the Solikamsk region, tremendous deposits of high-grade potash salts. The potash layers are located between the foothills of the Urals and the Kama River and cover an area of 2,000 square kilometers. The top stratum consists of carnallites ($KCl \cdot MgCl_2 \cdot 6H_2O$) and the lower of sylvinite ($KCl \cdot NaCl$).

The Academy of Sciences USSR, the Geological Committee, the GIPKh, UNIKhIM, NIU, and others, immediately took part in the solution of this important and interesting problem. Investigations showed that the salts of the upper Kama deposits contain bromine, cesium, and rubidium, in addition to chlorides of potassium, sodium, and magnesium. The first potash shaft in the USSR was sunk at the end of 1927. To overcome the difficulties and dangers involved, because of the solubility of the salts, the method of cementation was used in cutting the first pit and that of deep freezing was used in cutting the second pit.

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A large industrial and cultural center has been created at the mine during the five-year plans. The mines and a large chemical concentrating plant work continuously and at high capacities.

In addition to the large potash-salt deposits in the northern Urals, there are other potash-bearing regions, in the Carpathians, Urals (Emba region), Central Asia, and others, which add to the tremendous potash reserves of the Union, already several times greater than all the other world deposits.

As a result of the addition of the western Ukraine, the reserves of potash salts now include the deposits of the eastern Carpathians, which comprise two large districts, Kalushsko-Golynsk and Stebnikovsk.

In contrast to the Solikamsk potash salts, the Carpathian salts consist of aqueous and anhydrous chlorides and sulfates of potassium, sodium, calcium, and magnesium (kainite- $\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$, langbeinite- $\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$, polyhalite- $\text{K}_2\text{SO}_4 \cdot 2\text{CaSO}_4 \cdot \text{MgSO}_4 \cdot 2\text{H}_2\text{O}$, and others).

In 1932-1941, surveys and physicochemical analyses were made of the potash-magnesia deposits in the Caspian plain between the Volga, Ural, and Emba rivers, which had been discovered while drilling for petroleum in the southern part of the ancient Perm Sea. This large saltbearing region, rich in lakes and salt domes is of tremendous importance. Its study was begun under the direction of N. S. Kurnakov by the Institute of General and Inorganic Chemistry and is continued to this day by I. N. Lepeshkov, N. I. Buyalov, and others (I. N. Lepeshkov, Potash Salt of Volga-Emba and the Carpathians, 1946). The most important of the deposits is that of Ozinkov which is to the east of Saratov and to the northwest of Ural'sk. In addition to chlorides, these deposits contain sulfates, such as polyhalite and others, which had not been detected in the Solikamsk deposits. The analytical and geochemical data collected so far indicate that the salt deposits, including the potash salts, cover a very large territory of European USSR which had been inundated by the ancient Perm Sea. Salts have been discovered in the Moscow, Ivanovsk, Yaroslavl, Khar'kov, and other regions.

The supply of sulfuric acid required for the production of phosphatic and nitrogenous fertilizers is assured by the sources of raw materials discovered by the scientific research work carried out in the five-year plans.

The Soviet Union has inexhaustible and varied sources of raw materials for the production of sulfuric acid. These include mineral deposits, such as ordinary, carbonaceous, and flotation pyrites, sulfur and gypsum, as well as wastes from various branches of industry: coke, generator, and other gases containing hydrogen sulfide; waste gases from metallurgical furnaces and fuel gases containing sulfur dioxide; acid petroleum asphalt; pickling solutions, etc. As yet not all of the sources are utilized for the production of sulfuric acid.

Before the revolution, pyrite was imported from Spain, Norway, and Greece.

During the initial period of development of the Soviet sulfuric acid industry, the basic material for the production of sulfuric acid was domestic iron pyrite which was mined especially for this purpose. In recent years this iron pyrite has been replaced to a large extent by flotation pyrite and partly by carbonaceous pyrite, as well as by gases from metallurgical furnaces. Flotation pyrite is obtained as a waste in the concentration of poor copper-sulfide ore by flotation. The reserves of pyrite occurring as gangue in coal are considerably greater than those of ordinary pyrite. Furthermore, many new deposits of sulfur and sulfide ores have been surveyed in regions which heretofore had no raw materials for the production of sulfuric acid (for example, in Karelia, in the Central Asia Republics, etc.).

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Metallurgical and flue gases furnish a large amount of raw materials for the production of sulfuric acid, thus solving problems in connection with the utilization of sulfur from the sanitary and hygienic viewpoints. Important studies have been carried out with a view toward concentrating the sulfur dioxide coming from flue and metallurgical gases.

The NIUIF, UNIKHIM, VUGI, and other institutes have mastered the technique of burning sulfur and various types of sulfides in the laboratory and in pilot-scale installations. An investigation was made of the process of burning in mechanical furnaces of pyrrhotite and pyrite-pyrrhotite ores, large deposits of which have been found in the North and in other regions of the country. Conditions have been investigated for the regeneration of sulfuric acid from pickling solutions in metallurgical and machine industries by removing the ferrous sulfate from these solutions and decomposing it. Methods have been developed for the decomposition of acid petroleum asphalt (waste in the refining of petroleum which contains 20 to 50 percent H_2SO_4) to sulfur dioxide and coke breeze.

The studies carried out in the USSR make possible the utilization of various kinds of raw materials for the production of sulfuric acid.

The reserves of raw materials for the nitrogen industry, the largest branch of the Soviet chemical industry created during the existence of the Soviets, are no less extensive.

The country has tremendous resources of various kinds of coal, coke, peat, and natural and industrial gases, which assure the development of the nitrogen industry. The Soviet Union occupies second place in the world in coal reserves, and most of these reserves were discovered during the post-revolutionary period.

The reserves of "white coal" are also tremendous. At present, the "Large Volga" is being developed. The development of the tremendous energy resources of the Angara, Yenisey, and other rivers in Siberia and Central Asia will be undertaken next, and this will expand the electrochemical production of hydrogen, the electrothermal manufacture of phosphorus, and other industries.

The Soviet Union has organized a powerful coke chemical industry which supplies coke and purified coke gas to nitrogen fertilizer plants and to plants engaged in basic organic synthesis which use hydrogen, methane, ethylene, and other components.

In the last 10 years, the large resources of natural gases, which contain 90 to 99 percent methane and which constitute the raw material for the production of hydrogen by cracking or by conversion with steam, have also acquired great importance. Thanks to the development of hydroelectric power, electrolytic hydrogen (from water) is being used for the synthesis of ammonia.

It is then obvious that the Soviet nitrogen industry has all the fundamental sources of raw material for its successful development with the use of any methods for the production of hydrogen: by conversion of water gas, low-temperature cooling of coke gas, electrolysis of water, from steam and other methods.

In recent years, boron-containing ores have been added to the agronomical ores. Domestic boron raw materials were unknown in prerevolutionary Russia; all the requirements of the country were covered by imports of boron minerals and boron products from abroad. The import of these products practically ceased in 1917. A small amount of borax (4 to 6 tons per year) was produced from domestic volcanic mud of the Kerch and Taman peninsulas. The content of borax in the mud did not exceed 0.6 percent and the total amount of B_2O_3 did not exceed one percent.

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In 1958 a geological party of the NIUIF surveyed igneous deposits in the Caucasus, that is, datolite ($2\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$), containing up to 2.5 percent B_2O_3 . Boric acid has been produced from this relatively poor raw material at the NIUIF experimental plant for 2 years. At the same time, the question was raised of utilizing, as a source of raw borates, boron silicate ores, tourmalines, and tourmaline tailings obtained after the extraction of rare metals from the complex tourmaline sulfide ores, large deposits of which are available in the country. However, both datolites and tourmalines contain very small amounts of boron and require rather complex processes for their treatment.

The problem of finding supplies of raw borates was solved in 1954 by the discovery of borate deposits in the Ural-Emba region (TaNIGRI). At present, this deposit supplies all the Soviet plants with boric acid. The basic boron carriers in this deposit are asharite, $2\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$, and hydroboracite, $\text{CaO} \cdot \text{MgO} \cdot 3\text{B}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$. The rapidly growing requirements for boron products demand further studies for the discovery of new, and the expansion of known, boron deposits, as well as of the maximum utilization in industry of poor borates (by prior concentration) and even of some of the water found in petroleum drilling.

Hence, the vast geological research and mining surveys, with a view to assuring sufficient supplies for the fertilizer industry under the Soviet regime, resulted in the discovery of deposits of raw materials which guarantee the production of all types of basic fertilizers in unlimited quantities.

Phosphorus Fertilizers

Basic methods for the conversion of phosphorus-containing ores to fertilizers, partly realized in the USSR and partly earmarked for exploitation in a industry within the next years, may be divided as follows:

1. Grinding of phosphorites for the production of phosphorite meal;
2. Decomposition of natural phosphates with H_2SO_4 , E_2PO_4 , HNO_3 , and HCl for the production of superphosphate and concentrated fertilizers (enriched and double superphosphate, ammophos, nitrophoska, and others);
3. Thermal decomposition of phosphate by sintering or fusion with soda, lime, sodium sulfate, magnesite and alkali silicates, and other compounds for the production of so-called thermophosphates;
4. Thermal reduction of phosphates and volatilization of phosphorus with subsequent conversion of the phosphorus to phosphoric acid and its salts;
5. Treatment of phosphates with steam or hydrocarbons at high temperatures, in which the fluorine is removed and the phosphate is transformed into a form available to plants.

Each of these methods places different requirements upon the quality of the raw materials. For example, the acid method, particularly the production of superphosphate, requires a material of a higher grade than that suitable for thermal methods.

The use of ground phosphorite as a fertilizer had the attention of Russian and foreign investigators in the 1870s and 1880s, with Prof A. N. Engel'gardt as its most staunch defender. However, the opinions of the scientists and practitioners differed regarding the efficiency of these fertilizers. The NIU (A. N. Lebedyantsev and his collaborators) studied this problem very thoroughly from the very beginning of the Institute. Since the effectiveness of ground phosphorite depends to a great extent upon the properties of the soil, the main questions investigated dealt with the study of soils in which the use of ground phosphorite would be feasible, and also of the forms of phosphates and the suitable grain size.

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Pot and field tests have shown that ground phosphorite is effective not only in the zone of podsol soils, but over the entire northern half of the chernozem region of European USSR. In recent years the southern limit for the use of ground phosphorites has been moved still further south. It was found advisable to use ground phosphorite in the subtropical red soil of Georgia and in the saline soil of the left bank of the Volga which will be irrigated and ameliorated. Tests over many years have shown that all over the tremendous region of acid soils in the USSR, neutral and alkali forms of phosphates (phosphorite, thermophosphate, basic phosphate slags) are preferable to water-soluble acid modifications (superphosphate, ammophos, and others). Ground phosphorite is most effective when introduced into fallow soils under various crops. It is effective not only for grain crops, but also for such crops as flax, beets, hemp, potatoes, vegetables, tea, tangerines, etc. It is of interest to note that, after phosphorite has been introduced into the soil, it has a continued favorable effect on all plants of a rotation and even on several rotations. For example, in the experimental station of the NIUIF (podsol soil), phosphorite introduced in 1923 was still effective in 1943, that is, 20 years later, and on all the crops of a 6-field rotation. Analogous conditions were observed by many other experimental stations in various sections of the country. A very important conclusion may then be drawn: the effect produced by the introduction of phosphorite and superphosphate containing equal amounts of P_2O_5 may be considered to be equivalent. It was found, however, that this effect was produced by sedimentary phosphates but not by volcanic phosphates (crystalline apatite).

The use of ground phosphorite in the USSR before World War II was the largest in the world. The increase in the production of ground phosphorite requires a rapid development of phosphorite deposits and the erection of plants for the concentration and grinding of the ore.

Production of Superphosphate

During the past 30 years the production of superphosphate in the Soviet Union underwent considerable changes both with respect to quality and quantity. The first superphosphates produced in the years 1918 to 1922, using the just-discovered Vyatka and Yegor'evsk phosphorites, had very poor physical properties. The product contained only 10 to 12 percent available P_2O_5 which reverted in storage; the moisture in the product was as high as 18 to 20 percent; it consisted of pasty lump, which were difficult to spread; many consumers refused to accept the superphosphate and there were many conflicts between plant management and consumers. Gradually, by means of prior concentration of poor phosphorites and addition of bone meal, the amount of available P_2O_5 in the superphosphate was increased to 14 percent and its physical properties were improved.

In 1929 the NIUIF received the first samples of a new phosphatic raw material, Khibin apatite, and a new era in the development of phosphates set in. The new raw material was thoroughly investigated by the Institute from every possible angle.

It was found that the physical and chemical properties of apatite ore differed markedly from those of organogenic phosphorite. Laboratory experiments showed that it was impossible to produce superphosphate from nonconcentrated Khibin ore by the customary methods. Only flotation Khibin apatite could be used for that purpose. After a large concentration plant had been erected at the mine, all superphosphate plants began to use flotation apatite, and it soon moved to first place as a basic raw material in the production of superphosphate. The quality of the superphosphate product increased markedly. It should be noted that, in the treatment of apatite, a large amount of sulfuric acid is saved in comparison to the amount required in the conversion of phosphorites.

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In 1930 a few boatloads of apatite ore were shipped abroad as an experiment. Foreign plants, which had been used to treating rich sedimentary phosphorites, did not at first correctly evaluate the apatites, and as a result the reports of the majority of the firms regarding the use of Khibin apatite were negative. One large chemical concern wrote: "These natural phosphates are entirely unsuitable for the production of superphosphate." Another foreign firm reported: "Both local and foreign plants have tested the Mikhmansk phosphate and come to the conclusion that this material is entirely unsuitable for the superphosphate industry." Only after it became known that all Soviet plants were using apatite with great success, did the foreign firms and experts change their opinion.

The unsatisfactory results obtained abroad in the production of superphosphate from apatite are explained by the fact that the foreigners assumed the Khibin apatite to be a phosphorite of organogenic origin, without studying it as a special mineral of a different composition and a different structure.

The incorrect amounts and concentrations of sulfuric acid, the inadequate grinding of the apatite, and the nepheline and other minerals present in it, gave a low-grade product of unsatisfactory physical properties. Only after the members of the Institute carried out model experiments in a number of countries, and in various plants and laboratories, was the production of superphosphate from apatite recognized to be possible. The introduction of Khibin apatite into the fertilizer industry was carried out by the NIU and by various plants with the collaboration of L. E. Berlin, A. I. Shereshevskiy, A. A. Sokolovskiy, L. B. Grinshpan, N. N. Postnikov, and others, under the general direction of S. I. Vol'fkovich.

During the five-year plans the production of superphosphate continued to increase. The Stakhanovite movement which reached the superphosphate plants in 1935-1936 tremendously increased the productivity. At that time it had been considered necessary to keep superphosphate in storage for at least 30 days, but the dimensions of the plant warehouses prevented an increase in production. Enlargement of the existing storage space, however, would have required considerable capital expenditure. This difficulty was solved by the NIUIF scientists and by the plant workers. They carried out a number of measures which permitted curtailing the storage of superphosphate to one half or one third of the time, with simultaneous improvement of the properties of the superphosphate. The most important of these measures were: the use of larger amounts of sulfuric acid (70-72 parts per 100 parts of apatite by weight) with subsequent neutralization of the excess acidity by adding small amounts of readily decomposable phosphates to the superphosphate sent to storage; prior treatment of the superphosphate in storage, that is, loosening or dispersion of the superphosphate when dumped into storage, and shoveling during storage, in order to dry and to accelerate the curing of the phosphates; finally, more accurate proportioning of the reagents. As a result, the properties of the superphosphate improved, the amount of available P_2O_5 increasing from 18.7 to 19.5 percent.

In connection with the discovery of vast phosphorite deposits in the Kara-Tau Mountains, A. I. Shereshevskiy determined in his experiments at the NIUIF that this phosphorite was suitable for the production of superphosphate. It was found advisable to use concentrated phosphorite. The method of concentration is at present being worked out at the GIGKhS. A large number of superphosphate plants which will use Kara-Tau phosphorites will be constructed in Central Asia within the next few years.

Numerous investigations at the NIUIF of the decomposition kinetics of phosphate minerals by acids and the physicochemical analyses in the field of sulfuric acid treatment of phosphates have brought a great deal of clarity into the production of superphosphates. These studies were the first to show that after 2 1/2 hours of curing, as well as on further storage, anhydrous calcium sulfate and not gypsum, as had been assumed both in the USSR and abroad, is the sulfate portion of superphosphate.

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It was found that a correct operation of the process requires continuous feeding and rapid stirring of the reactants. Continuous feeding is particularly necessary, when concentrated sulfuric acid is used to permit mixing in the presence of large amounts of phosphoric acid. Higher homogeneity of the superphosphate, more complete elimination of the fluorine, and replacement of heavy physical labor by less heavy labor at the most dangerous locations, are then assured.

Of great importance is a method of continuous production of superphosphate in which not only the feeding is continuous but chambers with continuous charging of the raw material and continuous discharge of the superphosphate are used. This method will permit further acceleration of the process, improvement of working conditions, and a decrease in the cost of production. E. K. Lopatin, N. K. Firshtenberg, E. N. Zhuchkov, A. A. Sokolovskiy, and E. N. Ginzburg, among other investigators worked on the development of the process for the continuous production of superphosphate.

Some plants will use the so-called "ammonization" of superphosphate, that is, saturation of the superphosphate with ammonia or ammoniates (ammonium nitrate, urea, etc.) In this process, the ammonia reacts with the free phosphoric acid and monocalcium phosphate, present in the superphosphate, and forms ammonium and calcium phosphates. The nitrogen content of the product obtained in the treatment with ammonia is as high as 3 percent. Ammoniated superphosphate has excellent physical properties.

In the beginning, the Soviet superphosphate plants did not utilize the fluorine gases liberated during production. At the end of the First Five-Year Plan, only three plants had installations for the absorption of fluorine gas, and the recovery of sodium fluosilicate did not exceed 2 kilograms per ton of superphosphate. However, by 1936-1937 all superphosphate plants were equipped with installations for the recovery of fluorine, and at the end of 1937 the recovery of sodium fluosilicate in some plants was as high as 3.5 to 4 kilograms per ton of superphosphate; in some plants it was even higher (as a result of studies by the NIUIF and various plants; I. I. Zaring among others).

The improvements in the absorption installations increased the coefficient of absorption of fluorine gas to between 95 and 96 percent. The recovery of sodium fluosilicate then also increased.

Methods for the production of concentrated fertilizers, such as ammophos, dicalcium phosphate precipitate, double superphosphate, etc., have been devised and verified in plant operation. This is of great importance to the Union with its unlimited expanse and large transportation network.

In addition to the NIUIF, the members of Giprokhim and of many plants, including F. T. Golovanov, I. I. Karataev, D. L. Tayrlin, P. F. Derevitskiy, S. E. Uss, V. S. Demin, and A. I. Senger, took part in the development of the production of superphosphates and concentrated fertilizers.

Production of Phosphoric Acid

It is known that phosphoric acid is an intermediate product in the production of concentrated phosphorus fertilizers. The NIU devised a method which has already been carried out in several plants: the phosphate is first dissolved in circulating phosphoric acid; later or simultaneously, the calcium ion is precipitated with sulfuric acid; the precipitate formed, the so-called "phosphogypsum," is separated from the phosphoric acid solution in vacuum filters.

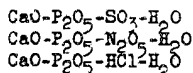
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Numerous investigations have been made of the physicochemical side of the processes for the treatment of natural phosphates with sulfuric, nitric, and hydrochloric acids. The equilibria of the quaternary systems



have been investigated (A. Belopol'skiy, A. Taperova, S. Shpunt, M. Shul'gina, and M. Serobrennikova).

Of particular interest is the first of these systems which is involved in the production of superphosphate, phosphoric acid, double superphosphate, dicalcium phosphate precipitate, etc. The existence limits for the stable and metastable solid phases, which are in equilibrium with the solutions of the given system at various temperatures and concentrations of phosphoric acid, have been determined. Particularly important to practical exploitation was the detailed study of the calcium sulfate modifications which precipitate from solutions under different conditions. It was found that under the conditions, at which superphosphate and phosphoric acid are produced, the first phase to precipitate is always the metastable hemihydrate, $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$. At a corresponding temperature and phosphoric acid concentration it later passes into the stable salt. Depending upon the locations of the solubility curves of anhydrite, CaSO_4 , the hemihydrate, $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$, and gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, this conversion proceeds in different ways and at varying rates.

In addition to the physicochemical analysis of the solubility of the system $\text{CaO-P}_2\text{O}_5\text{-SO}_3\text{-H}_2\text{O}$, an investigation was made of the kinetics of mutual conversion of the various forms of calcium sulfate in the presence of phosphoric acid. The polythermal diagram of the "isochronism" of the latent period of conversion was obtained as a result. This diagram was the theoretical foundation for the derivation of many new methods for the production of concentrated phosphoric acid and superphosphate of high P_2O_5 concentrations. The rates of crystallization of monocalcium phosphate from supersaturated solutions of the system $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$ were investigated.

The solubility curve of the dicalcium phosphate, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, metastable at 40 degrees centigrade, was investigated within the limits of the same system (M. I. Chepelevetskiy and others). A number of specific inhibitors of the transition of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ to the anhydrous salt was found on the basis of general concepts regarding the factors which influence the kinetics of crystallochemical conversions. In particular, the iron ion which improves the filterability of the precipitate is such an inhibitor. It is known that phosphates of trivalent metals, particularly iron, play a negative part in the acid treatment of phosphates. The systems $\text{Fe}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$, $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$, and $\text{Fe}_2\text{O}_3\text{-P}_2\text{O}_5\text{-SO}_3\text{-H}_2\text{O}$ were investigated in this connection (E. B. Brutskus and others). These studies determined the limiting ratio of iron oxide and phosphorus anhydride in the ore, beyond which rapid crystallization of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ sets in and interferes with the treatment of these ores.

In a number of studies dealing with the physicochemical analysis of salt and acid-salt systems, the time of reaction was assumed to be an equivalent coordinate in the composition-property diagram of the system. The equilibrium relations and kinetics have thus been correlated, and this is of great importance to industrial exploitation. Inasmuch as crystallization is the dominating process in the production of fertilizer salts, an investigation was made of the factors which influence the habit and the size of the crystals (A. V. Kazakov, M. I. Chepelevetskiy, and others). It was found that, depending upon the excess of one or the other component in the crystal lattice, as well as upon temperature, acidity of the medium, and presence of foreign cations, gypsum crystals of various shapes and dimensions are obtained. The optimum conditions for the production of crystals of the isometric form, which are

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most readily separated from the liquid phase, were determined. An investigation was also made of the effect of impurities on habit and the formation of druses in the precipitation of dicalcium phosphate, calcium carbonate, and other salts.

The production of macrocrystalline calcium sulfate precipitates, which are readily filtered and washed, from the mother liquor (phosphoric acid solution), has been perfected. The separation of phases was investigated in various apparatuses: rotating drum filters, band vacuum filters, and by continuous decantation and countercurrent washing in thickeners.

An optimum method of production was devised on the basis of the numerous investigations, and increases in the concentration of phosphoric acid and decreases in the amount of impurities, such as Fe, Al, SO_3 , F, and Si, were obtained (S. Vol'fkovich, A. Sokolovskiy, S. Voskresenskiy, R. Remen, I. Gofman, M. Kobrin, N. Kryuchkov, A. Ionass, and many others).

Experience has shown that the best raw material for the production of phosphoric acid by extraction is apatite flotation concentrate. It was found in laboratory experiments that phosphoric acid may be extracted from ground phosphorite of the Chulak-Tau deposits. Aktyubinsk, Vyatka, Trukhachev, and some other flotation concentrates were also found to be suitable for the production of phosphoric acid. The properties and compositions of phosphoric acid prepared from various phosphatic raw materials are listed in Table 1.

Table 1. Composition of Phosphoric Acid Prepared from Various Types of Phosphatic Raw Materials*

Material	P_2O_5	SO_3	Fe_2O_3	Al_2O_3	F	$\frac{\text{SO}_3}{\text{P}_2\text{O}_5} \cdot 100$	$\frac{\text{Fe}_2\text{O}_3}{\text{P}_2\text{O}_5} \cdot 100$
Khlebn flotation apatite	22-26	1-2	0.6-1.1	0.3-0.9	1.3-1.6	4-7	2.4
Yegor'evsk flotation phosphorite	22-25	2.5-3.8	2.3-2.8	No data	No data	11-15	9-12
Vyatka washed phosphorite	19-22	4-5.5	2-3.5	1-1.2	0.9-1	21-26	9-17
Vyatka flotation phosphorite	22-25	2-3	1.6-2.1	0.7-0.8	0.9-1.1	9-12	7.9

*Data from A. I. Shereshevskiy, "Production of Phosphorus Fertilizers," Results of Studies for the Years 1939-1944, NIUIF, Goskhimizdat, 1946.

Phosphorites containing large amounts of Fe_2O_3 are unsuitable, unless they are highly concentrated by calcination, flotation, etc.

In the production of phosphoric acid by extraction, 1.4 to 1.6 tons of waste (phosphogypsum) is obtained per ton of phosphate treated. The NIUIF (R. Simanovskaya) devised methods for the conversion of phosphogypsum to construction materials of the type of plaster and molding gypsum, anhydrite cement, etc. Tests of these materials by construction organizations gave entirely satisfactory results. Another way of utilizing phosphogypsum, by treatment with ammonia and carbon dioxide (or ammonium carbonate) for the production of ammonium sulfate, was investigated at the NIUIF in 1928-1934 by S. Vol'fkovich, V. Kamzolkin, A. Sokolovskiy, S. Perel'man, and others.

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In the process of extraction, about 10 percent of fluorine goes into solution, and 20 percent F is liberated into the gas phase as SiF_4 and HF ; the rest remains undecomposed in the phosphogypsum. The removal of fluorine is of great importance to the further treatment of the acid. The Institute worked out and introduced into industry a method for the removal from the phosphoric acid of 75 to 90 percent of the fluorine present in the raw material. The method is based on the relatively low solubility of the alkali salts of hydrofluosilicic acid in the presence of alkali ions in the phosphoric acid at temperatures below 40 degrees centigrade. Salts of Na, K, or Ba are introduced into a technical phosphoric acid solution containing H_2SiF_6 as chlorides, sulfates, nitrates, carbonates, phosphates, etc.

The NIIEP also investigated the removal of rare earths in the extraction of phosphoric acid from apatite concentrate containing 1 percent rare earths.

In Soviet plants the concentration of phosphoric acid obtained by extraction does not exceed 20 to 25 percent P_2O_5 . The concentration is insufficient for the use of the acid in the production of concentrated fertilizers, such as double superphosphate, ammonphos, etc. Methods and conditions were therefore investigated for the evaporation of phosphoric acid to a concentration of 35 to 50 percent P_2O_5 .

The laboratories of the Institute studied the amounts and the compositions of the residues accumulated in the evaporation of phosphoric acid from various types of raw materials, the heats of evaporation of water from phosphoric acid solutions, the viscosity of the solutions, and many other properties. Vacuum evaporators with natural and forced circulations (NIIEP design), evaporators heated with fuel gas, and others were tested on a pilot-plant scale.

The conditions for the utilization of fluorine liberated in the evaporation of phosphoric acid (I. L. Gofman and others), the corrosion of metals during evaporation, etc., were also investigated. In recent years the NIIEP has been studying processes for the direct production of highly concentrated phosphoric acid (40-50 percent P_2O_5), without evaporation, from apatite concentrates and from Kara-Tau phosphorites (S. K. Voskresenskiy, S. K. Milovanova). Satisfactory results were obtained with apatite concentrates. Conditions have been investigated for the formation of crystals of the hemihydrate and anhydrous calcium sulfate, which approach the spherical form and which can be readily filtered and washed.

Concentrated Fertilizers

Many years of laboratory study, later verified in plant operation, have been devoted to the production of concentrated fertilizers. It should suffice to mention that the studies for the production of one of the most widely used concentrated fertilizers, double superphosphate (product of decomposition of natural phosphate with phosphoric acid), were carried out with natural phosphates from all the known Soviet deposits. The studies included methods using phosphoric acid of various concentrations (extracted, evaporated, thermal), ammonization of the product, etc. (S. Voskresenskiy, T. Milovanova, R. Lerner, L. Berlin, and others).

Three basic methods were checked in plant operation: (1) a method analogous to the production of ordinary superphosphate with subsequent drying of the double superphosphate; (2) drying of the superphosphate slurry in a rotary drum for the production of a granulated product by grinding, screening, and return of the fines to the cycle; (3) a method in which the phosphate and the phosphoric acid are mixed for a prolonged period of time in a horizontal mixer (log-washer type) with a conveyor belt instead of a drum.

Experimental studies have shown that, for the production of double superphosphate from low-grade phosphorites, it is advisable to use flotation material.

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only. The composition of double superphosphate obtained from various types of raw materials is given in Table 2.

Table 2. Composition of Double Superphosphate Prepared From Various Types of Raw Materials*

<u>Material</u>	<u>P₂O₅ Total</u>	<u>P₂O₅ Availability</u>	<u>P₂O₅ water Solubility</u>	<u>P₂O₅ Free</u>	<u>H₂O</u>	<u>Fe₂O₃ P₂O₅</u>
Phosphoric acid from flotation apatite; composes Vyatka phosphorite	44-45	44-44.5	39.5-40.3	5.0	8	5.4
Phosphoric acid from 50% apatite plus 40% washed Vyatka phosphorite; de- composes washed Vyatka phosphorite	45.7	44.6	38.4	5.0	8	7.8
Vyatka flotation phos- phorite, in both stages of the pro- cess	41.0	40.0	36.1	3.5-5.5	8	7.5
Khibin flotation apa- tite, in both stages of the pro- cess	46.8- 49.2	47.1- 49.2	44.3- 48.3	6.8- 10.8	5.5- 10.0	

*Data from article by A. I. Shereshevskiy cited above.

A method for preparation of another concentrated fertilizer, ammophos, was worked out by Soviet experts and used in industry before World War II. Ammophos is prepared by saturating phosphoric acid with ammonia; it consists essentially of monoammonium and diammonium phosphate and small amounts of other salts. It has excellent physical properties and is very effective in agriculture. In the production of ammophos from extracted phosphoric acid by the optimum method, the phosphoric acid is evaporated to a concentration of 35 to 40 percent P₂O₅; the evaporated acid is saturated with ammonia gas or liquid ammonia; the product obtained is dried, ground, and screened, and the finely ground ammophos is returned to the dryer. The conversion of low-grade phosphorites of primary concentration meets with operating difficulties. The quality of the finished product is inferior to that prepared from flotation concentrates or mixtures of these concentrates with phosphorites of primary concentration. Ammophos contains 12 to 20 percent N and 45 to 54 percent P₂O₅.

Many physicochemical investigations were made of the equilibrium systems of P₂O₅-SO₃-NH₃-H₂O (L. Berlin, B. Mantsev, and others) in addition to studies covering the industrial production of ammophos (S. Vol'fkovich, V. Kamzolkin, R. Remen, S. Voskresenskiy, N. Kryuchkov, G. Strongin, and others).

The chemistry and technology of the concentrated fertilizer, dicalcium phosphate precipitate (product of neutralization of phosphoric acid with lime or limestone), were investigated thoroughly. The studies included the quantitative ratios of the reactants, the rate of reaction of phosphoric acid with lime or limestone, the temperatures required for precipitation and drying, and the conditions for the crystallization of dicalcium phosphate, its filtration, phase conversion, and dehydration during drying, etc. (E. Briška, S. Dragunov, A. Sokolovskiy, M. Kobrin, M. Chepelevetskiy, and others). In industry dicalcium

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phosphate precipitate is obtained by treatment of apatite and phosphorite with sulfuric acid. When apatite concentrate is used for the treatment with lime, with precipitation of the fluorine from the acid, the product contains 38.5 percent total and 37 percent citrate-soluble P_2O_5 . The product obtained from Aktyubinsk phosphorite and limestone, without precipitation of the fluorine from the solution, contains 32.4 percent total and 30.4 percent citrate-soluble P_2O_5 .

In recent years NIUIF (I. Gofman, A. Sokolovskiy) devised new methods for the production of dicalcium phosphate precipitate, tricalcium phosphate for use as a feed supplement; these products do not contain any harmful components (fluorine, arsenic, etc.) and are of great importance in the raising of livestock.

As is known, the national economy requires technical and pure phosphoric acid salts in addition to phosphorus fertilizers. A large amount of experimental and plant-operation data has been accumulated on the production of many phosphates: disodium and trisodium phosphates, hexametaphosphates, manganese phosphates, pure ortho-, pyro-, and metaphosphates of calcium, sodium, ammonium, and aluminum, melamine phosphates, etc.

Of particular importance to the Soviet industry are the methods devised by the NIUIF for the nitric acid conversion of natural phosphates to phosphorus and nitrogen fertilizers. The characteristic feature of this process is the absence of waste and the double action of the nitric acid: the acid decomposes phosphate and becomes a constituent of the final product, the nitrate fertilizer. This is its advantage in comparison with sulfuric and hydrochloric acid treatment of phosphates.

D. N. Pryanishnikov first proposed the use of nitric acid in the decomposition of phosphates in 1908, but the process was not introduced into industry until 1925-1926 after thorough studies and after the synthesis of ammonia had been mastered.

Of the many variations possible in a process starting with the decomposition of phosphates with nitric acid, devised at the NIUIF, two methods deserve attention: (1) production of dicalcium phosphate precipitate and calcium nitrate by neutralizing the phosphoric acid mixed with calcium nitrate by means of lime or limestone; the product obtained contains as much as 45 percent available P_2O_5 ; (2) production of ammonium nitrate and ammonium phosphate by removing the calcium from the mixture of phosphoric acid and calcium nitrate with ammonium sulfate, and subsequent neutralization with ammonia and regeneration of the phosphogypsum and ammonium carbonate or ammonia and carbon dioxide (S. Vol'fkovich, A. Dolyak, A. Loginova, and others).

In recent years, the NIUIF has been investigating methods for simplifying the direct production of nitrogen-phosphorus-potassium fertilizers, the composition and properties of which would meet the requirements of agriculture.

Of major interest to the Soviet Union is a method in which a part of the calcium nitrate, 40 to 60 percent of the amount present in solution, is removed from the nitric acid extract by moderate cooling to about 10 degrees centigrade. As a result of the removal of the calcium nitrate, the P_2O_5/Ca ratio in solution increases approximately twofold. After removal of the calcium nitrate the solution is neutralized with ammonia in two or three stages. The result is a nitrogen-phosphorus fertilizer composed essentially of $CaHPO_4$, NH_4NO_3 , small amounts of $(NH_4)_2HPO_4$ and $2Ca(NO_3)_2$, and of $CaCO_3$ impurities. If HCl is added to the product of the first step before drying, a triple fertilizer of the type of nitrophoska is obtained instead of a double fertilizer.

The method for the treatment of natural phosphates with hydrochloric acid devised at the NIUIF, chiefly for the treatment of Khibin apatite and Vys'ke phosphorite, is feasible only when cheap waste hydrochloric acid is available.

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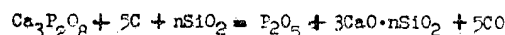
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It is impossible within the scope of this paper to discuss the various other interesting studies relating to the conversion of low-grade ferruginous phosphorites to salts and fertilizers. Numerous investigations were made by the NIUIF of calcination, chlorination, and so-called "GALA" decomposition of phosphorites, and of the introduction of various salts to decrease the oxides of iron, aluminum, etc., in the solution.

Thermal Conversion of Phosphates

Generally, thermal methods for the conversion of phosphates are based on the reduction of phosphates with carbon at 1,300 to 1,400 degrees centigrade, and higher, according to the equation:



Thermal methods are used both in the Soviet Union and foreign countries. Studies of phosphorus volatilization were undertaken in the USSR at the initiative of E. Britske and have been carried out for many years under his direction at the NIUIF. They are particularly suitable for regions where cheap electric power is available.

Experiments on the electrothermal volatilization of phosphorus from phosphorites were initiated in the USSR by S. I. Vol'fkovich and E. I. Zhukovskiy in 1921-1922. The data derived by them were used for the construction of the first electric furnaces.

The rapid electrification of the country heightened the interest in the electrothermal volatilization of phosphorus with its subsequent conversion to concentrated fertilizers.

The scientific work and industrial exploitation were carried out by members of the NIUIF and plant technicians. In addition, N. N. Postnikov (NIUIF), B. K. Klimov, B. Rakovshchik, T. Shikhutskiy, N. P. Fedot'ev, and others of the GIPKh, together with M. D. Senilov, N. N. Znamenskiy, A. N. Shubnikov, A. I. Vilesov, I. I. Orlov, E. I. Uflyand, and other employees of phosphate plants contributed to the study and exploitation of the electrothermal process.

As a result of these studies, three-phase electric furnaces for the volatilization of phosphorus were installed in several plants with a view to testing phosphates from different deposits.

The method for blast-furnace volatilization of phosphorus, proposed and developed by E. V. Britske, was tested in pilot-plant operation, but had not been worked industrially, chiefly because of the high consumption of coke. Nevertheless, in 1941, due to the critical demand for phosphorus, the blast-furnace method was operated in several plants, although the yield of phosphorus was low. Extensive series of theoretical and experimental studies in this field were carried out by N. E. Pestov, A. I. Shereshevskiy, A. M. Malets, M. N. Bolotin, and other collaborators of E. Britske. Later, I. C. Rotenkants contributed several studies and calculations.

Investigations were carried out relating to the condensation of phosphorus from phosphorus-containing gas, determination of the viscosity and density of molten phosphorus, oxidation of phosphorus, and absorption of the phosphorus acid mist. These studies contributed methods for the industrial production of thermal phosphoric acid containing as high as 85 percent P_2O_5 in one-step and two-step operations.

Methods for the purification of commercial, thermal phosphoric acid, devised on the basis of the studies carried out at the NIUIF (E. E. Zasser and others), led to the organization of an industry for the production of pure acid.

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chemically pure phosphoric acid. Simultaneously with the investigation of the conversion of phosphate, the NIIF (N. I. Postnikov and others) studied the by-products and wastes of this production, that is, ferrophosphorus, slag, and dust. The method for the treatment of ferrophosphorus by fusion with lime and lime, proposed and developed by A. M. Malets, is of interest. The phosphorus in this process is oxidized by the oxygen of the ore and, combining with the lime, forms calcium phosphate of the type of Thomas slag. Simultaneously a high-grade steel of the type of "Armco" is obtained. The slag contains about 30 percent P_2O_5 , 27 percent of which is citrate-soluble. The steel contains traces of phosphorus.

A group of NIIF members (N. W. Postnikov, I. S. Rozenkrants, B. I. Levi, and others) devised methods for the complete purification of gases liberated in electric volatilization and containing in addition to carbon, harmful impurities, such as phosphine, etc., with the aid of various oxidizers and sorbents. The use of the purified gas is recommended in the production of methanol and formates, and in other organic syntheses, as well as for the production of hydrogen and other purposes.

Of considerable interest are the methods developed in recent years for the thermal conversion of natural phosphate by means of steam at about 1,350 to 1,400 degrees centigrade, in which fluorine is eliminated and the phosphate is converted to a citrate-soluble form (A. I. Shereshevskiy). Like results are obtained from calcination of superphosphate or natural phosphate, treated with sulfuric or phosphoric acid, at lower temperatures (I. Gofman and R. E. Oshakovich). The products of this treatment may be used both as fertilizers and as feed supplements. The proposed construction of power plants and the use of hydroelectric resources on a large scale favor the development of the thermal production of phosphoric acid and its salts.

Thermal Treatment of Phosphates with Alkalies

The decomposition of phosphate with alkali compounds at high temperatures, 1,100 - 1,350 degrees centigrade attracted the attention of Soviet scientists, largely because it makes possible the production of "thermophosphates" from more concentrated apatite-nepheline ores and some low-grade phosphorites, particularly when these operations are combined with alkali treatment of other ores (for example, extraction with lime of aluminum oxide from nepheline) or fusion with soda. Fusion of phosphates and alkalis or alkaline earth compounds yields products having a formula close to $(CaO)_3 \cdot (Na,K)_2P_2O_5 \cdot CaO \cdot SiO_2$.

The conditions for the production of thermophosphates by means of heating natural phosphate with soda and sodium sulfate are the most thoroughly investigated in the USSR (S. I. Vol'fkovich, S. S. Perelman, A. I. Shereshevskiy, and others). The authors determined that a thermophosphate containing about 30 percent available P_2O_5 may be obtained from apatite concentrate. A. B. Bekasov of the Kazakh Affiliate of the Academy of Sciences investigated the preparation of thermophosphates by heating Kara-Tau phosphorites with sodium sulfate and soda.

A. I. Shereshevskiy and K. I. Zayverkin heated natural phosphates with lime basic blast furnace slag, or natural magnesite or dolomite, and obtained phosphorus fertilizers of the type of Thomas slag containing 16 to 18 percent of citrate-soluble P_2O_5 . In recent years encouraging studies in this direction were carried out under plant conditions by S. N. Melent'ev and A. A. Izmass under the direction of E. B. Britske with the cooperation of the workers of the "Apatite" plant. The industrial exploitation of the processes for the production of thermophosphates has been limited for reasons technical and economic reasons, but the processes will soon be carried out in practice, particularly in the northern regions of the USSR.

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Nitrogen Fertilizers

The production of nitrogenous compounds by the fixation of atmospheric nitrogen did not exist in prerevolutionary Russia. There were a few small installations operating under the Valentiner system which produced nitric acid from imported Chilean nitrate. The capacity of these plants in 1915 was 49,000 tons of nitric acid. The extraction of ammonia from coke-oven gas was negligible; many coke ovens had no absorption installations.

During World War I, the first attempts were made to produce nitric acid by the oxidation of ammonia extracted from coke-oven gas, and the first plant for the oxidation of ammonia on the basis of Russian investigations was erected in the Donbas (I. I. Andreev and others).

At present, the nitrogen industry has developed into the most important branch of the chemical industry, supplying agriculture with large quantities of fertilizer.

The scientific research work paralleled the continuous growth of the nitrogen industry. Vast experience has been gathered in these years on the production of synthetic ammonia, of ammonia as a by-product of the coke industry, and its conversion to nitric acid and nitrogenous fertilizers.

The State Institute of the Nitrogen Industry and the workers of the nitrogen plants made valuable contributions to the design of equipment and to further improvement in the production of fixed nitrogen and its compounds.

Without going into the many interesting problems which have been solved, and which must be investigated further, in connection with the production of synthetic ammonia and its oxidation to nitric acid (these problems will be discussed in a separate paper), mention is here made only of the fundamental studies and the achievements in the production of nitrogen fertilizers.

For the past two decades the largest portion of the ammonia fertilizers supplied to agriculture by the Soviet industry has been in the form of pure ammonium nitrate, whereas in foreign countries ammonium nitrate has been regarded largely as an intermediate product which had to be mixed with other fertilizers. The USA began to use ammonium nitrate as a separate fertilizer as late as 1944. Because of its high nitrogen concentration (35%) and its physiological properties, ammonium nitrate is an excellent fertilizer, but its unsatisfactory physical properties (high hygroscopicity and tendency to cake) interfere with its effective utilization in agriculture. Soviet investigators have therefore endeavored to improve the physical properties of ammonium nitrate, and in this they partly succeeded. Intensive study and exploitation of satisfactory methods of production of ammonium nitrate in industry were carried out at the same time. In these investigations Soviet institutes and plants introduced a number of new ideas and at some points surpassed the scientific concepts of capitalistic countries. In the first plants, the heat of reaction of ammonia and nitric acid (in the formation of a solid product from gaseous NH_3 and HNO_3 , +34.7 calories are liberated) was not utilized. The ammonium nitrate solution was evaporated to a concentration not higher than 85 percent; crystallization was carried out in cumbersome and inefficient equipment. The finished product contained a large amount of moisture and had poor physical properties.

Radical changes and improvements in the production of ammonium nitrate have been made in recent years. The design of a neutralizing apparatus which operates under atmospheric pressure and utilizes the heat of reaction has been evolved after prolonged research (D. Epshteyn, M. Viktorov, A. Murzin, V. Kharke, and others). At present all the Soviet plants are equipped with these apparatuses. The evaporating systems have also been radically reconstructed. All the plants are provided with evaporators of very high capacity designed by the Giprokrot. The ammonium nitrate solution is evaporated to a concentration of

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96.5 percent NH_4NO_3 . The method of producing granulated ammonium nitrate on a large scale, by spraying in towers while in a molten state, has also been solved in practice by the studies of the NIUIF, Giproazot, and various plants (A. Dubovitskiy, A. Filinov, Z. Lunskaia, F. Margolis, and others). The methods for decreasing the hygroscopicity and caking of ammonium nitrate have been improved. These studies determined the physicochemical conditions which favor the humidification and caking of ammonium nitrate temperature, humidity of air, effect of crystalline modification, and other conditions of production and storage. The effects of additions, the introduction of which improves the properties of ammonium nitrate, and the optimum temperature during operation, have been investigated. The addition of hydrophobic compounds which form a surface film, such as paraffin, petroleum residues, bitumen, etc., decreases considerably the hygroscopicity of the material and the rate of absorption of moisture from the air (I. Krichevskiy, A. Dubovitskiy, F. Margolis, and others). The best results are obtained when granulation and coating of the particles with a hydrophobic film are combined with powdering of the particles with conditioning substances, such as kaolin, diatomaceous earth, ash, etc.

The study of the changes in the crystalline structure of ammonium nitrate as a function of heating and cooling conditions is of particular importance.

It was found in a study carried out by the method of cinematic microphotography (S. Vol'fkovich and T. Glasova) that ammonium nitrate obtained by rapid cooling (quenching) has a dense structure and does not cake excessively. Furthermore, methods have been studied for using ammonium nitrate as a component for the production of complex fertilizers (nitrophoska, potassium-ammonium nitrate, calcium-ammonium nitrate, and other mixtures), for further improvements in the construction of neutralizers, evaporators, crystallizers, granulators, and for better utilization of the heats of reaction and crystallization.

A foundation was laid for the production of another popular type of nitrogen fertilizer, ammonium sulfate. The most rapid development took place in the production of ammonium sulfate from ammonia recovered from coke-oven gas. The use of synthetic ammonia is less feasible; synthetic ammonia should preferably be combined with nitric acid for the production of ammonium nitrate.

Considering the disadvantages of the customary method for the production of ammonium sulfate, the so-called "wet" method, in which ammonia is reacted with sulfuric acid in saturators, the production of ammonium sulfate by the "dry" method has been mastered. This method is based on utilizing the heat which is liberated in the reaction of atomized sulfuric acid with ammonia gas. The same idea was utilized in the experimental study of the NIUIF for the production of mixtures of ammonium sulfate, ammonium phosphate ("sulfocarnophos"), and dry ammonophos. The NIUIF finished its work on devising a method for the production of ammonium sulfate from gypsum and phosphogypsum.

The USSR has tremendous deposits of gypsum, which makes the utilization of the sulfate portion of these deposits of great practical interest. No less desirable is the utilization of the wastes (phosphogypsum) which accumulate in the production of phosphoric acid by decomposition of phosphate with sulfuric acid, provided ammonia and carbon dioxide are available in the neighborhood. The conversion of gypsum was accomplished by two methods, gas and liquid. In the gas method, the calcium sulfate reacts with gaseous ammonia and carbon dioxide; in the liquid method it reacts with ammonium carbonate solution. Experiments at the NIUIF plant showed the superiority of the liquid method, because the equipment required is much simpler.

Another source of raw material for the production of ammonium sulfate has been investigated. This is mirabilite (natural sodium sulfate) which is available in tremendous quantities in the Gulf of Kara-bogaz-gol, in the lakes of the Kulundin steppe, in the Aral Sea, and many other localities. In 1930 the NIUIF (S. Vol'fkovich, A. Belopol'skiy and collaborators) began a systematic study of the process of converting sodium sulfate with ammonia and carbon

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dioxide to two valuable products, soda and ammonium sulfate. (In contrast to the Solvay process in which ammonium chloride is obtained and later treated with lime for the regeneration of ammonia). Laboratory investigations were concerned with the study of a number of equilibrium salt systems of direct practical importance to the new ammonia-soda process.

Many studies covered the carbonization kinetics of ammonia-sulfate solutions and the dynamics involved in the variation of titers during carbonization. The studies also included the partial pressures of ammonia, carbon dioxide, and water vapor over ammonia-sulfate solutions of various degrees of carbonization, the treatment of mother liquors after carbonization, and various details of the process. A method, whose various important points were checked under semiplant and plant conditions, was devised by laboratory studies. The advantage of this method over the customary soda process (using NaCl) is the complete absence of waste; between 90 and 95 percent sodium sulfate and 96 to 99 percent ammonia are recovered in this process.

The production of the most valuable nitrogen fertilizer, urea, which contains 45 percent N, has been organized on the basis of numerous laboratory and plant studies carried out by the GIVD, NIUIF, and various plants (B. Bolotov, A. Popova, B. Levi, V. Orlov, N. Rubinshteyn, E. Bomshteyn, and others). In addition to being a very valuable fertilizer, urea is used in the production of plastics, chemical and pharmaceutical products, and for many other purposes. It has not been easy to surmount all the difficulties connected with the production of urea. It was necessary not only to devise the method of operation, but to design the equipment, and to prevent high corrosion of the apparatus parts. All these problems were solved satisfactorily. The work related to improving the equipment and the methods is being continued with a view to reducing the cost of production. The manufacture of urea will undoubtedly continue to expand in the Soviet Union.

Among various other types of nitrogen fertilizers, calcium cyanamide must be mentioned. It is an effective fertilizer for cotton, sugar beets, and other commercial plants. Considering its value as a fertilizer and as a raw material for the production of cyanide compounds, a plant has been erected for the production of the required quantities of calcium cyanamide.

Sodium and potassium nitrates are effective fertilizers for a number of commercial crops. Sodium nitrate is particularly beneficial to sugar beets. In the Soviet Union it is produced in nitric acid plants by the absorption of nitrous gases with soda. A new method is being developed for the production of sodium and potassium nitrates from sodium or potassium chloride and nitric acid or nitric oxides (D. Speteyn, V. Nikolaev, B. Vasil'ev, and others). This will increase the source of supply for sodium and potassium nitrates and will save on soda and caustic potash required for their production. A thorough investigation has also been made of the process for the production of potassium nitrate by conversion of ammonium nitrate with potassium chloride in an alkali medium (F. G. Margolis, NIUIF) and of other methods related to the production of nitrate salts.

The scientific institutes procured all the pertinent data on the operating conditions and for improving the physical properties of calcium nitrate (V. Klevke, A. Murzin, I. Krichovskiy, and others). Calcium nitrate is most effective in the acid soils in many regions of the country. Ammonium phosphate, which is a highly concentrated fertilizer and which has been discussed in the section dealing with phosphate fertilizers, must be added to the various nitrogen fertilizers discussed above.

Potassium Fertilizers

For a number of years prior to the discovery and survey of the gigantic Upper Kama (Se'lkamsk) deposits of potash salts in 1925-1926, many attempts had been made to produce potassium salts from sea water (A. I. Khablukov, D. Sayirshcheyn, and others), natural aluminum silicates, feldspathic ores,

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glauconite, etc. (A. Danakov, S. Vol'fkovich, A. Pyranichnikov, and others), vegetable ash, and some potassium-containing industrial wastes.

After the tremendous reserves and the high quality of the Solikamsk potash salts became known, the NIU under the chairmanship of N. S. Kurnakov arranged for conferences with representatives of many chemical institutes and laboratories to work out an over-all plan and to set the closing dates for various scientific research; a potassium research bureau was established to correlate the work. As a result of the intensive studies of various investigations -- among whom the work of the laboratory of the Northern Chemical Trust at Bratkovsk (F. Vol'f, N. Yfremov, V. Yalov, and others) was particularly outstanding -- of the Academy of Sciences (N. S. Kurnakov and his collaborators), of the GIKKh (D. Manoev, A. Bergman, and others), and on the basis of foreign literature, the scientific council of the Khimstroil approved plans for the construction of a potassium chloride plant which was to be one of the largest and most modern plants of the chemical industry.

After the production of potassium chloride from sylvinite had been mastered, many other industries were developed at the potassium combine for the combined utilization of sylvinite and carnallite (D. I. Shcherbakov, S. Z. Makarov, Ya. M. Kheyfets, and others). Furthermore, many valuable investigations were made with a view to increasing production and improving the properties of the final products (A. S. Leontichuk, Ya. E. Vil'nyanskiy, R. Ya. Manisl', and others).

The NIU and other institutes studied various methods for the production of potassium sulfate, nitrate, and phosphate, and triple fertilizers containing potassium (Z. V. Britske, S. I. Vol'fkovich, E. P. Pokryvalinskaya, R. E. Remen, F. G. Margolis, and others).

In recent years preparations have been made for the forthcoming exploitation of potash salt deposits other than those at Solikamsk. The IONKh and the Institute of Halurgy investigated the compositions and methods of treating potassium salts in the near-Ural and Emba regions, western Ukraine, and others.

Several investigations were concerned with the physicochemical study of the pertinent equilibrium systems and of the reaction kinetics (A. G. Bergman, E. I. Akhmedov, D. B. Vasil'ev, A. P. Belopol'skiy, K. P. Aleksandrov, S. Ya. Shpunt, and others), and with devising a more rapid and more accurate method for the analysis of potassium in fertilizers and salts (S. N. Rozanov, B. S. Dregunov, and others).

Agrochemical experiments at the NIU, VTUAK, and a number of other organizations determined the effectiveness of various forms of potassium fertilizers, and the requirements for them in various regions and by various crops.

As mentioned earlier, after the western Ukraine had been added to the Union, the Stebnite and Kalush potash enterprises, which treat sulfates in addition to chlorides, became a part of the Soviet potassium industry. A large potassium combine is being erected for the exploitation of upper Kama deposits.

Boron and Other Fertilizers

The importance of boron, as well as that of many other microelements (that is, elements present in very small quantities in the vegetation and in the soil), in plant life has been definitely established by agricultural chemistry, particularly within the last 15 years. Up to 1935, when the Soviet Union imported both boron raw materials and boron products, and only a negligible amount was produced from poor raw material, Kurch volcanic mud, there was no base for the production of boron fertilizers. It was only in 1935-1936 after the discovery of the Indorsk deposits of readily decomposable borates in

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the Ural-Emba region, that it has become possible to develop the domestic production of boron and its salts. The methods devised at the NIUIF for the conversion of datolites from the Northern Caucasus and tourmalines from Siberia, which are difficult to decompose and contain very little boron, were discarded after the new borates had been discovered. The Soviet boron industry now uses the latter material exclusively.

Several plants for the treatment of Indersk borates, largely with sulfuric acid, are now in operation as a result of the studies at the NIUIF (L. E. Berlin, V. T. Mikerov, and others), at the Institute of Metallurgy (V. E. Grushvitskiy and others), and by industry (A. N. Kostyukovskiy and others).

Acid, alkali, thermal, and combined methods for the conversion of borates to boric acid and borax were investigated. At the same time methods were studied for the production of phosphorus and combined fertilizers containing boron, as well as means for the utilization of the by-products, chiefly magnesium sulfate, and the wastes.

Many physicochemical and geochemical problems were also investigated (A. V. Nikolaev and A. G. Kurnakov, IONKh; V. E. Grushvitskiy, Institute of Metallurgy). Many studies were made by the NIUIF, VIUAA, and several other institutes, on the physiological and agrochemical importance of boron as a plant nutrient (N. N. Khalizov, N. V. Katalymov, E. V. Bobko, E. I. Pospelov, and others).

For the near future, construction of new boron plants and expansion of the sources of raw materials, by including poor borate ores and, possibly, insoluble natural boron silicates are planned.

Many studies in the USSR have been concerned with other microelements, such as manganese, zinc, copper, radioactive elements, growth hormones (heterocaring) and herbicides. A part of these studies is now being checked under plant conditions.

It was mentioned earlier that industry has mastered the production of several complex and mixed fertilizers. It is planned within the next few years to expand the assortment of double, triple, and perhaps even quadruple fertilizer mixtures, which would give to the plants the required amounts of nitrogen, phosphorus, potassium, boron, etc. The production of fertilizers containing peat and mobile forms of phosphoric acid and nitrogen is proposed for several soils (red soil, sandy soil, etc.).

It is impossible within the scope of this paper to discuss other fertilizers, such as limestone, gypsum, peat, industrial and agricultural wastes, and the so-called "green fertilizers" (leguminous plants), since they are not a part of the fertilizer industry. It should be mentioned, however, that Soviet agrochemists have carried out many studies in this field and that these have contributed greatly to national agriculture.

Chemical Analysis and Control in the Production of Fertilizers

Investigations of chemical analyses and methods of control in the production of fertilizers have occupied an important place in the studies of USSR scientific institutes and plant laboratories. The largest number of investigations has been concerned with phosphorus-containing materials. Analysis of phosphates may now be referred to as one of the chapters of analytical chemistry. Only the most important achievements in the chemical analysis of fertilizers will be enumerated below.

The following methods have been worked out: volumetric method for the determination of P_2O_5 , including acidimetric titration; colorimetric methods for the determination of P_2O_5 , Fe_2O_3 , SiO_2 , F, and other elements; new methods for the determination of meta- and pyrophosphate ions; improved methods for the

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quantitative determination of fluorine; rapid volumetric-bromometric methods for the determination of ammonia nitrogen; and a number of rapid methods for the determination of boron, magnesium, and sulfate ions, among others (S. N. Rozanov, G. A. Markova, M. L. Chepelevetskiy, E. B. Brutskus, B. B. Evlina, V. A. Kazarinova, R. E. Osherovich, B. V. Mikhail'chuk, B. I. Levi, T. A. Kryukova, E. E. Zusser, and many others).

The polarographic method of analysis in the production of acids and salts has come to the fore in recent years (T. A. Kryukova, E. N. Popova, and others).

Many studies were made to determine the physicochemical and commercial properties of fertilizers: drillability, caking, hygroscopicity, granulometric composition, etc. (N. Pestov, N. Khait, F. Baranov, and others). Handbooks have been published for the control of the superphosphate and other productions (M. Chepelevetskiy, E. Brutskus, and others). Many studies have been concerned with determining the various physicochemical constants of chemically pure acids and salts.

Many studies are available on the application of the new automatic methods of control in gases and liquids (GIAP, NIUIF, Karpov Institute, and others). These include automatic regulation of the liquid level and the density of the slurry, automatic control of the feeding of gases and liquids into reaction vessels, etc.

The survey of the fertilizer industry would be incomplete without mention of the progress made in the production of sulfuric acid which, from the inception of the mineral fertilizer industry to this very day, has been a fundamental prop of the phosphate industry and is connected by a number of threads to nitrogen fertilizers, as well as to the boron industry.

Sulfuric Acid

The production of sulfuric acid in prerevolutionary Russia was at a low level. The raw material for most plants was imported from abroad. Tsarist Russia occupied 13th place in world production of sulfuric acid. Pyrite furnaces were manually operated in most of the chamber plants. The average rate of the chamber volume was 4 to 5 kilograms per cubic meter per day; the sulfuric acid was concentrated in lead or porcelain vessels with external heating. A plant erected during World War I was more modern: it contained an Oppel chamber system, systems with tangential chambers, Kessler apparatus, and Caillard equipment.

Contact plants were at a much higher technical level. The Tentelovsk system devised by the chemists of the Tentelovsk plant (now the "Red Chemist" Plant) was one of the most modern systems at the time. It should be noted that contact acid constituted more than half of all the sulfuric acid produced in Russia. In the first years after the revolution, the production of sulfuric acid decreased markedly because of the closing of many plants. During the reconstruction period many old plants were rebuilt and expanded. By 1928 the production of sulfuric acid reached 200,000 tons as compared to 17,000 tons in 1919.

A huge sulfuric acid industry was organized in the first and second five-year plans. By the end of the Second Five-Year Plan the Soviet Union occupied fourth place in world production of sulfuric acid.

The sulfuric acid plants were of the latest design and were equipped with the most modern tower and contact systems, as well as with Kessler and Chemtec concentrators, and with vacuum apparatuses. All tower and contact plants were equipped with powerful furnaces, centrifugal acid-resistant pumps, electric precipitators, etc. Apparatuses of original design and high capacity, devised by Soviet experts, were introduced: contact apparatuses for the oxidation of

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sulfur dioxide (design of G. K. Borekov and N. P. Sosnovskiy), high-capacity absorption precipitators with all the pertinent equipment ("Gas Purifier" Trust), high-capacity iron coolers, etc. While during the First Five-Year Plan the plants tried to reach their estimated capacity, during the Second Five-Year Plan the capacity of the tower and contact systems was increased. This fruitful work was begun, and is continued to this day, by the large collective of workers of sulfuric acid plants and of the MKhTI, NIUIF, Giprokhim, UNIKhIM, and other institutes. Early in 1935 many tower plants reached a capacity of 26 to 37 kilograms per cubic meters instead of proposed capacity of 18 to 20 kilograms per cubic meters per day. The Stakhanov movement created favorable conditions for the further development of the system. Soon several plants operated at a rate of 100 kilograms per cubic meters (Vinnitskiy plant and others), and in some plants a rate of 200 kilograms per cubic meters was reached at various periods. To prevent the deterioration of the lead equipment under the increased rate of operation, lead was replaced by materials stable under these conditions, notably cast iron, iron, and others.

A great deal of work was done by the NIUIF, UNIKhIM, and various plants to increase the production of mechanical furnaces. In 1936-1937 the production of VKhZ and Wedge furnaces was increased to 200 kilograms per cubic meters of furnace hearth per day, and in the subsequent years a rate of 200 to 250 kilograms per cubic meters has been maintained by many plants. During the same period the estimated capacity of furnaces for the pulverulent calcination of flotation pyrites (flotation tailings) has been exceeded, and the burning in these furnaces of moist tailings (containing up to 5 percent moisture) has been mastered.

A method for cooling the acid by decreasing the cooling surface to approximately one half has been worked out in the plants. Until recently the tower systems yielded an acid of 75 to 76 percent H_2SO_4 . Studies at the NIUIF contributed a tower process which yields oil of vitriol directly.

The contact process for the production of sulfuric acid also underwent great changes in the postrevolutionary period. It is sufficient to mention that the capacity of individual contact installations increased fivefold. These fundamental changes became possible owing to the great improvements made in the contact process. The replacement of platinum catalysts by more efficient and more stable vanadium catalyst masses gave very satisfactory results (Odessa Institute of Applied Chemistry, MKhTI, NIKhTI, NIUIF). The time of contact of the gas in the catalyst zone has been decreased and at the same time the yield increased to 97 percent. The Soviet plants are equipped with converters of domestic design which have a high capacity and a high coefficient of gas utilization (G. K. Borekov, N. P. Sosnovskiy, N. M. Levin, and others).

In recent years a process has been used in which oil of vitriol is introduced from the side, and this increases the yield of fuming sulfuric acid by 150 to 200 percent of the gas capacity of the converter.

The evaporators have also been considerably improved, largely by raising the temperature of the heating gases (A. I. Kirsh, S. P. Rozenskoy, N. I. Belzer, A. P. Samarin, N. A. Kazantsev, and others).

Special mention must be made of an extensive theoretical study carried out in connection with the development of processes for the production of sulfuric acid. For example, B. D. Mel'nik and others at the LKhTI, and K. M. Malin and others at the NIUIF, were the first to make a theoretical study of the conditions for the calcination of pyrites in order to increase the capacity of the furnaces. A great number of studies (V. N. Shul'ts and others, MKhTI; K. M. Malin and others, NIUIF; I. N. Kuz'minykh, UNIKhIM; S. D. Stupnikov and others, Giprokhim) have been concerned with the investigation of the "nitroses" process. These investigations contributed very important improvements and opened a way for increasing the efficiency of tower systems. Particularly promising is the use of oxygen in the production of tower acid. Thorough investigations covering

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the theory of the contact oxidation of sulfur dioxide, the collision kinetics on a vanadium catalyst, the methods of calculation, the design of new converters, the use of oxygen in contact operation, and many others were made by G. K. Borekov and his collaborators at the NIUIF. Valuable contributions on the absorption of sulfur dioxide and condensation of sulfuric acid were made by A. G. Amelin at the NIUIF.

Successful studies of the corrosion of materials were carried out by E. Yushmanov at the UNIKHIM and M. V. Vtorov at the NIUIF.

The experiments of G. K. Borekov, L. G. Ritter, and others at the NIUIF have shown that when oxygen is used the capacity of the converters may be increased substantially. The application of oxygen is particularly beneficial in the treatment of 100 percent sulfur dioxide gas obtained from the waste gases of nonferrous metallurgical furnaces. The use of oxygen permits the direct production of high-grade fuming sulfuric acid, sulfuric acid anhydride, and a number of other valuable products.

Exit gases of metallurgical furnaces, combustion chambers, etc., containing small amounts of SO_2 , furnish a tremendous and practically inexhaustible source of starting materials for the production of sulfuric acid. The problem of utilizing these gases is closely related to the problem of their enrichment. Many individuals and many organizations investigated these problems; B. I. Shmeerson, I. D. Pysakhov, S. Golyand, and others, NIIOGAZ; S. P. Rozenknop, N. E. Kirichenko, NIUIF; T. D. Averbukh and others, UNIKHIM.

Various methods for concentrating SO_2 were tested on a semiplant scale. The studies of various reagents to be used in these methods are being continued.

The inexhaustible sources of raw materials discovered and exploited by the Soviets and the excellent preparation that has been given to a large number of specialists guarantee the further development of the sulfuric acid industry.

Conclusion

At the First All-Union Conference of the workers of the socialistic industry held 4 February 1931, Comrade Stalin said: "We are 50 to 100 years behind the leading countries of the world. We must cover this span in 10 years. Either we accomplish this or we shall be crushed." This reference to the backwardness of our industry applied largely to the nitrogen, phosphate, and potassium industries.

At present, we may assert with pride that the Soviet fertilizer industry made tremendous strides in the five-year plans. The tempo of its growth exceeds anything heretofore known regarding the development of capitalist industries.

The war with fascism, which started 10 years after Stalin made the speech mentioned above, ended in a complete victory for the USSR, thus demonstrating the strength of the country and of the socialistic industry.

The prerevolutionary phosphate fertilizer industry amounted to only 2 or 3 percent of the present industry, while the nitrogen and potassium industry were developed within the last 20 years.

The USSR now occupies first place in world reserves of phosphate and potassium ores. Tremendous sources of raw materials for the sulfuric acid industry have been discovered, investigated, and put to use. Deposits of boron ores have been discovered and are being exploited. A mighty power base has been created for the development of electrochemical and electrothermal methods of production of fertilizers. The sources of raw materials and of electric power contribute to an unlimited development of the fertilizer industry.

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Not only has the import of agricultural ores and fertilizers been discontinued, but the country began to export considerable quantities of apatite, potash salts, and some types of fertilizers.

Large, complex, and modern plants for the production of synthetic ammonia, nitric acid and ammonium nitrate, sulfuric acid, superphosphate, and potassium chloride have been erected during the first and second five-year plans. New industries have been created: electrothermal production of phosphorus and phosphoric acid, and of concentrated fertilizers, such as ammophos, urea, dicalcium phosphate precipitate, and fertilizer mixtures. The Stakhanov movement and the improvement of processes on the basis of most modern achievements of science and technique contributed to a continued growth of the qualitative and quantitative indices of production and to a decrease in the production cost of fertilizers and sulfuric acid.

The large scientific research institutes and well-equipped plant laboratories, as well as many universities, carried out a large number of creative investigations which have been used as a basis for new processes as well as for the improvement of existing processes. The chemical, agricultural, geological, mining, and other institutes of higher learning prepared thousands of specialists who are now working in scientific and planning institutes, in mines, plants, and in agriculture. Before the revolution the number of specialists in these fields numbered only a few dozen.

In the past 30 years, in addition to several thousand research studies, there were published many monographs, textbooks, and handbooks which reflect the creative work and the experience gathered by Soviet science and technology in the fields of chemistry and the fertilizer industry.

In spite of the great achievements made by the Soviet fertilizer industry and agriculture, even more grandiose problems have to be solved within the next few years: it is imperative not only to reconstruct the industry destroyed by the fascist barbarians, but also to make rapid strides in the development of the fertilizer industry with the use of the most modern methods; it is necessary to study and develop new bases of agronomical ores; it is necessary to widen the variety of fertilizers, especially concentrated and complex fertilizers; it is necessary to build many new fertilizer plants, pits, and concentration plants.

Many new industries will be based on the most recent achievements of Soviet chemical science and technology.

The tremendous requirements which the expanding agriculture places upon the Soviet fertilizer industry and Stalin's statement that: "we must not only catch up with but surpass in the immediate future the achievements of science beyond the borders of our country," obligates the Soviet chemists to raise even higher the theoretical and creative level of their work and to make possible a more rapid exploitation of scientific achievements in industry.

Soviet chemistry has everything at its disposal to fulfill the traditions, exciting, and thankful tasks for increasing the productive capacity of the Soviet land and raising the prosperity of the peoples inhabiting our great country.

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